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Reducing the gel effect in free radical polymerization

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Abstract

The gel effect is a phenomenon that often takes place during a free radical polymerization at intermediate or high degrees of conversion. It consists of the autoacceleration of the rate of the polymerization and it is due to diffusion limitations that slow down the termination reaction leaving the propagation and the initiation reactions unaffected. This phenomenon is highly undesired in industrial application because it causes a fast and dramatic increase of the temperature of the reacting medium, often leading to scale-up problems, instabilities, hot spots, and erratic behavior. In this paper, we present the results of kinetic experiments performed in a cone and plate rheometer with two common monomers: styrene and *n*-butylmethacrylate. We show that the gel effect can be significantly reduced, if not eliminated, performing the polymerization at high shear rate. A new experimental device, the helical barrel rheometer, has been used and some preliminary results are presented.

Keywords: Gel effect; Rheometry; Reactive extrusion

1. Introduction

A free radical polymerization consists of three steps when secondary phenomena as chain transfer can be neglected: initiation, propagation and termination. In this case, the rate of polymerization is given by the following well-known expression (Odian, 1991):

$$R = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = \left(\frac{f k_\mathrm{i}}{k_\mathrm{t}}\right)^{1/2} k_\mathrm{p}[I]^{1/2}[M]. \quad (1)$$

The negative sign is added in order to have an intrinsically positive expression of the rate of polymerization. f is the initiator efficiency, k_i, k_p and k_t are the rate constants of the initiation, propagation and termination reactions, respectively, and $[I]$ and $[M]$ are the concentrations of the initiator and of the monomer.

This expression is valid in the initial stage of the polymerization, when the rates of the three steps are constant.

The gel effect is a major problem in a free radical polymerization. It consists of a fast and sudden increase of the overall rate of the process and therefore also of the viscosity of the medium and it occurs at intermediate or high degrees of conversion depending on the operating conditions.

The gel effect is due to diffusion limitations that hinder only the movement of the growing macromolecules, and not the movement of the unreacted monomer molecules. Therefore, only the rate constant of the termination reaction, which takes place when two growing macromolecules collide, decreases significantly, whereas the rate constant of the propagation reaction, which involves a reacting macromolecule and a small monomer molecule, remains unaffected. Thus, the overall rate constant of the polymerization increases.

When the gel effect takes place a large amount of heat is suddenly released, because free radical polymerization is a highly exothermic process. Since the medium is very viscous, the heat released by the gel effect is very difficult to remove. Therefore, a sudden and fast increase of the temperature of the reacting medium occurs.

Generally, the polymerization becomes too fast and too difficult to control. The process may also become unstable with subsequent disastrous consequences in terms of the quality of the product and of the safety of the process itself (Janssen, 1998). Industrial plants are often operated under conditions which are far from optimal, to minimize the risk of unstable behavior (Epstein & Pojman, 1999).

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Moreover, the gel effect is a major problem when trying to scale up polymerization processes. Heat transfer problems are easily avoided at the laboratory scale when the surface-to-volume ratio of reactors is high enough to control the temperature properly. This is no longer true in the industrial scale. Therefore, reducing the gel effect and/or being able to quantify it reliably is crucial in scaling up polymerization processes and in optimizing industrial applications. The scientific literature concerning the gel effect has been recently reviewed (O'Neil & Torkelson, 1997). Most papers try to determine the reason why the gel effect takes place on the molecular scale but not to influence it (Saban, Georges, Veregin, Hamer & Kazmaier, 1995). In this paper we present results showing that the gel effect can be reduced when the polymerization is performed at high-shear rates.

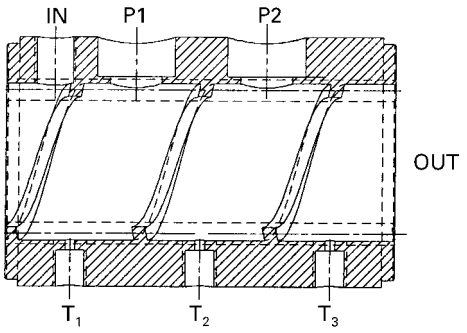

Fig. 1. A sectional view of the measuring part of the Helical Barrel Rheometer. The monomer–initiator solution is fed through the "IN" until it fills up the gap completely. The HBR is heated electrically and the heating system is connected to a control system. P1 and P2 are the positions of the pressure sensors. T1, T2 and T3 are the positions of three thermocouples used to check that the temperature of the sample is uniform across the whole rheometer. After the experiment the polymer is removed through the "OUT".

2. Materials and methods

2.1. Cone and plate

The isothermal increase of viscosity during a free-radical polymerization has been measured in a cone and plate rheometer (Brabender Co., Duisburg, Germany) at different shear rates and different temperatures. Styrene and *n*-butylmethacrylate have been tested. Trigonox 47S was used as initiator. The concentration of initiator was chosen so as to have an initial lag-time much longer than the time required by the medium to reach the operating temperature. Since the amount of reacting medium is small (~ 10 ml), it was possible to study the gel effect in isothermal conditions and only small oscillations ($\pm 1^{\circ}$C) around the set point were observed.

Sometimes the experiments were repeated in order to take samples at different times and analyze them by gel permeation chromatography (GPC) and neutron magnetic resonance (NMR). The qualitative increase of the average molecular weight and of the degree of conversion, respectively, was then determined.

2.2. The Helical barrel rheometer

The helical barrel rheometer (HBR), Figs. 1 and 2, is geometrically very similar to an extruder, i.e., to an apparatus that has already been used successfully in industrial applications. The only difference is in the fact that the tread is mounted on the barrel and not on the rotating element, in order to have more stable measurements (Todd, Gogos, Esseghir, Yu & Widagdo, 1997). It was built in the workshops of the University of Groningen.

The viscous flow in the helical channel of the metering section of a conventional extruder is generally characterized in terms of a volumetric drag flow, Q_d and a pressure

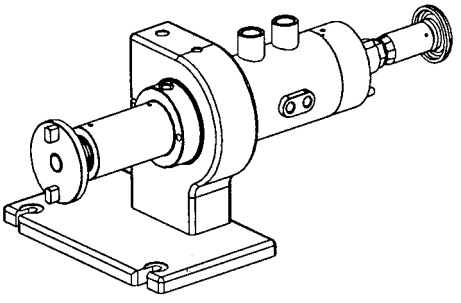

Fig. 2. A schematic diagram of the HBR as it looks from the outside.

flow Q_p:

$$Q_d = \pi D W h \cos\theta N/2, \tag{2}$$

$$Q_p = W h^3 \Delta P \sin\theta/12\eta L, \tag{3}$$

where N is the screw rotational speed, D is the screw diameter, W is the width of the channel, θ is the screw helix angle, h is the channel depth, ΔP is the pressure difference measured over the length L and η is the viscosity. At closed discharge, the drag flow and the pressure flow must be equal (and opposite), since the overall flow must be equal to zero. Therefore, the following relationship holds:

$$\eta = \Delta P h^2/6N\pi^2 D^2, \tag{4}$$

where ΔP is the pressure drop measured across one flight. It is easy to calculate the viscosity of the medium if the pressure drop is measured. Moreover, it is possible to perform experiments at different shear rates simply varying the rotational speed of the rotating element. The dimensions of the HBR were obviously chosen in order to measure high viscosities, corresponding to high conversions. Therefore, this HBR is not reliable at low

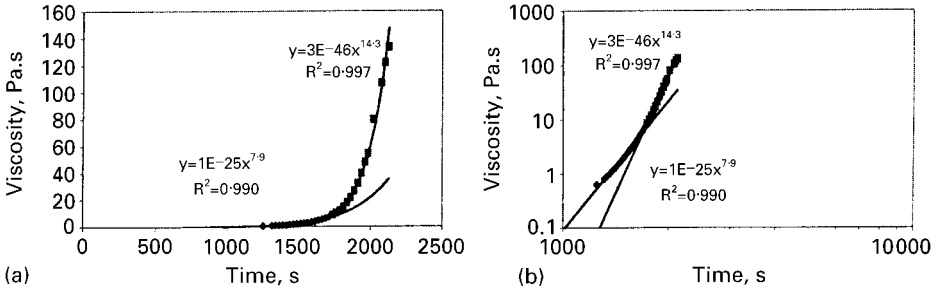

Fig. 3. The increase of viscosity during the polymerization of BMA in linear–linear (a) and log–log (b) coordinates. $T = 90°C$. Shear rate $30\ s^{-1}$.

viscosities and at the initial stage of the reaction, were, anyway, the gel effect is not expected to occur.

The HBR has two important advantages:

(1) It permits measurement of the increase of viscosity during a polymerization process in a configuration, which is similar to the extruder, a widely used industrial reactor.
(2) When the HBR is connected to a reactor, it is also possible to perform on-line measurements of the viscosity by pumping in the reacting medium (Macosko, 1994).

3. Results and discussion

3.1. Cone and plate

Many measurements have been performed in a cone and plate rheometer in different conditions of temperature, shear rate and initiator concentration, both for styrene and *n*-butylmethacrylate. One typical result of the many obtained is shown in Fig. 3. Whatever the operating conditions, the data of viscosity as a function of time were well fitted by a double-power-law trend of the increase of the viscosity with time. The exponent of the first part was always lower than the one corresponding to the second part. The borderline between the first and the second power law was chosen in order to optimize the fit. NMR measurements showed that the conversion is approximately 60% at the transition point.

These data are in agreement with the literature (Malkin & Kulichikhin, 1996) and show that at a certain point of the process the gel effects sets in and the viscosity increases at a higher pace because the rate of the polymerization is higher.

The difference between the two exponents can be considered as a measure of the extent of the gel effect.

Different series of measurements were performed at different shear rates keeping all the other experimental conditions the same in order to find out if the gel effect was somehow influenced by the shear rate at which the polymerization is carried out. In fact, the gel effect takes

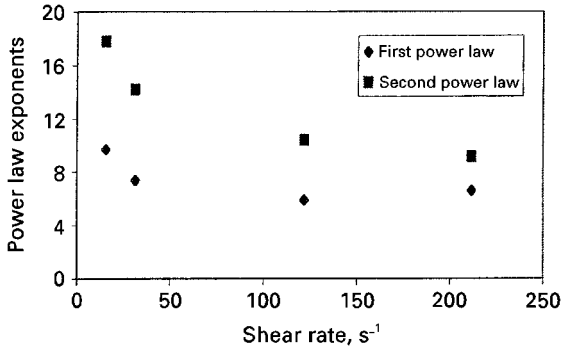

Fig. 4. Power-law exponents for the polymerization of BMA. $T = 110°C$.

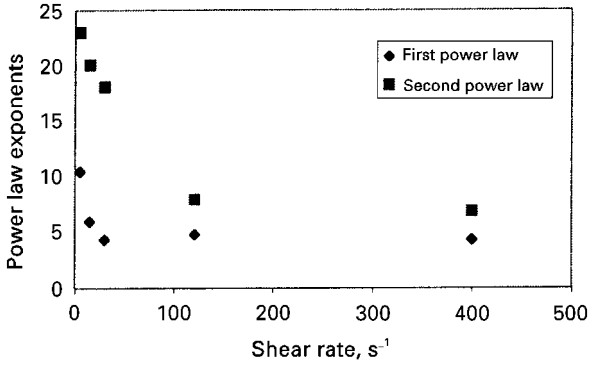

Fig. 5. Power-law exponents for the polymerization of styrene at 90°C.

place when the concentration of polymer is already high and the reacting medium must be considered as non-Newtonian.

Two series of measurements are plotted in Figs. 4 and 5. Other similar data were also obtained for different reacting conditions but they are not shown.

It is evident that the difference between the two exponents decrease if the shear rate increases. Therefore, the gel effect is reduced when polymerization is carried out at a higher shear rate. When the shear rate is higher than $200\ s^{-1}$, the increase of viscosity with time can also be

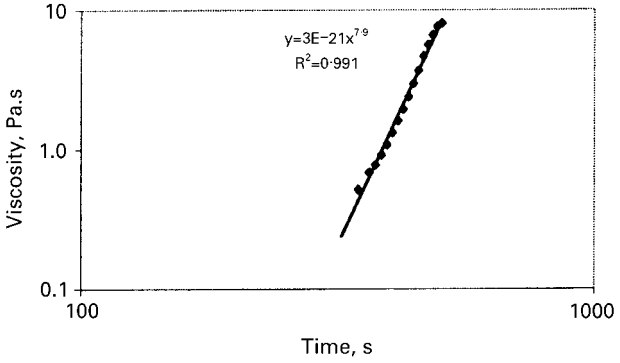

Fig. 6. The increase of viscosity during the polymerization of BMA at high shear rate (210 s^{-1}). $T = 110°C$.

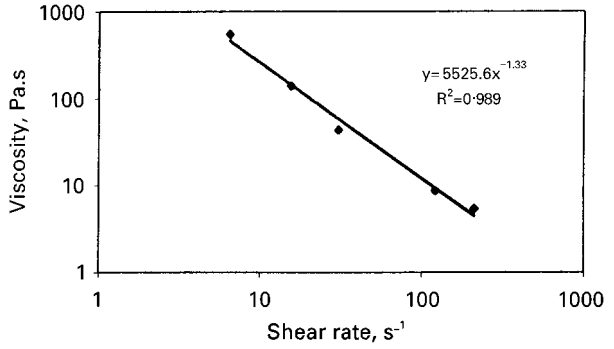

Fig. 7. Maximum viscosity for the polymerization of styrene at 116°C.

fitted by a single power law, showing that the gel effect can even be eliminated (Fig. 6).

Finally, the maximal viscosities obtained in each of the experiments performed at different shear rates and corresponding to almost complete conversion were plotted against the shear rate, Fig. 7. After the maximal viscosity, the trend became unstable and unreproducible. The reason for these irregularities is not clear yet and will be discussed in a subsequent paper. In the literature, they have been attributed to phase separation (Onuki, 1997; Onuki, Yamanoto & Taniguchi, 1997).

Those viscosities correspond to a conversion of about 90%, as shown by NMR analysis. A power-law trend of the maximal viscosities versus the shear rate can be seen. The exponent is smaller than -1; therefore the shear rate has a real influence on the gel effect, which cannot simply be attributed to the shear-thinning behavior typical of polymeric systems.

Finally, GPC measurements showed that during an experiment the average molecular weight is initially constant and then slightly increases with time after the onset of the gel effect. This result is in agreement with the literature and can be explained with the longer average lifetime of growing macromolecules due to the decrease of the rate of the termination reaction.

Table 1
Comparison of viscosity measurements obtained with cone and plate rheometer and with the HBR for two glucose syrup solutions

HRB (Pa s)	Cone and plate (Pa s)
0.21	0.19
0.39	0.41

3.2. Helical barrel rheometer

The most important property of the cone and plate rheometer is that the sample is subjected to the same shear rate in each point. This is the reason why the cone and plate rheometer is so widely applied in rheological research. On the other hand, this fluidodynamic homogeneity will be seldom encountered in real polymerization reactors.

The helical barrel rheometer is characterized by a complex velocity profile of the fluid inside the channel and different parts of the sample will be subjected to different shear rates. Nevertheless, the average shear rate is proportional to the speed of the rotating element.

This fundamental difference between the two rheometers used in this study makes the comparison of experimental results obtained with the two rheometers somewhat difficult and tricky.

Before performing polymerization processes inside the HBR, its reliability as viscometer was checked using a couple of glucose syrups diluted with water. These samples can be considered as Newtonian and therefore the viscosity data obtained with the two rheometers are not influenced by the shear rate and, thus, comparable.

The results obtained are showed in Table 1. They show a good agreement between the two measuring devices.

The viscosities obtained proved to be effectively independent of the velocity of the rotating element for both the rheometers.

Then the HBR was used as a polymerization reactor and the increase of viscosity with time was measured.

One result is shown in Fig. 8. Once again, a double power-law trend was found, similar, at least qualitatively, to the one obtained by cone and plate rheometer in similar experimental conditions.

This result is encouraging with a view to further use of the HBR in the study of the gel effect and of techniques aimed at limiting its negative effects. This would be of primary importance for developing enhanced polymerization processes on industrial-scale limiting the negative consequences of the gel effect. Nevertheless, more experimental data are definitively required before a quantitative comparison of the two rheometers can be made. Particularly, experiments will be carried out in the HBR at different velocities of the rotating element, i.e. different average shear rates, in order to find out if the results

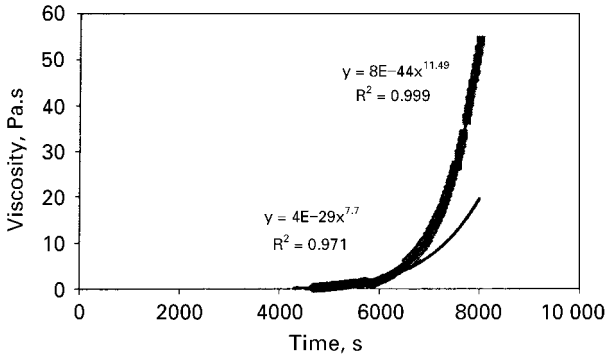

Fig. 8. The polymerization of BMA in the HBR. $T = 95°C$. Velocity of the cylinder: 0.1667 rot/s.

obtained with cone and plate rheometry are also valid for a geometric configurations which is more similar to the one of real reactors.

4. Conclusions

The gel effect is a major problem in free radical polymerization. The process, because of the gel effect, becomes too fast and difficult to control. The temperature increases suddenly and many problems may arise: instabilities, hot spots, and product with undesired properties. Two rheometers have been used in order to investigate how to reduce the gel effect. The cone and plate rheometer gave excellent results, showing that the gel effect can be reduced and eliminated if the polymerization is carried out at high shear rate.

Some preliminary results suggest that the same investigation can be extended to the helical barrel rheometer, which has the advantage of being very similar to an extruder and that can also be used for on-line measurements of viscosity during industrial processes.

References

Epstein, I. R., & Pojman, J. A. (1999). Nonlinear dynamics related to polymeric systems. *Chaos*, *9*, 255–259.

Janssen, L. P. B. M. (1998). On the stability of reactive extrusion. *Polymer Engineering and Science*, *38*, 2010–2019.

Macosko, C. W. (1994). *Rheology: principles, measurements and applications*. New York: VCH Publishers.

Malkin, A. Ya., & Kulichikhin, S. G. (1996). *Rheokinetics*. Heidelberg: Hüthig & Wepf.

Odian, G. (1991). *Principles of polymerization* (3rd ed). New York: Wiley Interscience.

O'Neil, G. A., & Torkelson, J. M. (1997). Recent advances in the understanding of the gel effect in free-radical polymerization. *Trends in Polymer Science*, *5*, 349–355.

Onuki, A. (1997). Phase transition of fluids in shear flow. *Journal of physics*, *9*, 6119–6157.

Onuki, A., Yamanoto, R., & Taniguchi, T. (1997). Phase separation in polymer solutions induced by shear. *Journal de Physique II*, *7*, 295–304.

Saban, M. D., Georges, M. K., Veregin, R. P. N., Hamer, G. K., & Kazmaier, P. M. (1995). Nitroxide-mediated free radical polymerization of styrene. Absence of the gel effect. *Macromolecules*, *28*, 7032–7034.

Todd, D. B., Gogos, C. G., Esseghir, M., Yu, D.-W., & Widagdo, S. (1997). Monitoring process viscosities with a new on-line rheometer. *Plastics Engineering*, *53*, 107–108.